ChemComm

COMMUNICATION

Check for updates

Cite this: Chem. Commun., 2018, 54, 5323

Received 19th January 2018, Accepted 17th April 2018

DOI: 10.1039/c8cc00459e

rsc.li/chemcomm

Highly efficient electrochemical ammonia synthesis *via* nitrogen reduction reactions on a VN nanowire array under ambient conditions[†]

Xiaoping Zhang, Rong-Mei Kong, Huitong Du, Lian Xia 🗅 and Fengli Qu 🗅 *

The development of a sustainable route to ammonia production is one of the most attractive targets in chemistry. The primary method of ammonia production, Haber–Bosch process, can bring about excessive consumption of fossil fuels and large CO₂ emission. In this communication, we develop a VN nanowire array on carbon cloth (VN/CC) as a high-performance catalyst for the nitrogen reduction reaction (NRR) under ambient conditions. Such an electrocatalyst achieves high ammonia yield ($2.48 \times 10^{-10} \text{ mol}^{-1} \text{ s}^{-1} \text{ cm}^{-2}$) and faradaic efficiency (3.58%) at -0.3 V versus RHE in 0.1 M HCl, outperforming most reported results for N₂ fixation under ambient conditions, and even comparing favorably with those obtained under high temperatures and/or pressures. This work not only provides us an attractive catalyst material for the NRR in acidic media, but would also open up an exciting new avenue to the rational design and fabrication of transition metal nitrides for the NRR.

Ammonia (NH₃) is among the chemicals produced in the largest quantities in the chemical industry, where it is primarily used in the production of fertilizers.^{1–5} The ammonia-based fertilizer is predominantly synthesized *via* the industrial Haber–Bosch process.^{6,7} In this process, its synthesis is heavily relied on high temperature and pressure (350–550 °C, 150–350 atm) of the Haber–Bosch process, wherein the input of H₂ and energy is largely derived from fossil fuels and thus results in a large amount of CO₂ emission.^{8–13} Accordingly, more sustainable and economical alternatives for ammonia production will be demanded to reduce greenhouse gas emission.

Many alternative methods to synthesize ammonia have been proposed in recent years, such as enzyme-catalyzed synthesis, photochemical synthesis, and electrochemical synthesis.^{14–20} Although the electrochemical syntheses of ammonia *via* the nitrogen reduction reaction (NRR) have been successfully achieved, there are still a lot of defects, including relatively low

yield, expensive electrolytes and harsh experimental conditions and so on. It is striking to note that the electrochemical synthesis of ammonia has been regarded as the most favourable route because it can be realized under ambient conditions based on heterogeneous catalysts.²¹ To date, noble metal catalysts, such as Au and Ru, have shown superior catalytic activity for the electrochemical synthesis of ammonia.^{22,23} Yan and co-workers reported that Au sub-nanoclusters on TiO₂ act as an efficient electrocatalyst for the NRR, which exhibit high ammonia yield (21.4 μ g h⁻¹ mg_{cat}⁻¹) and faradaic efficiency (8.11%) at room temperature and atmospheric pressure. However, the noble metal catalysts suffer from low abundance and high cost, hindering their large-scale application. Moreover, theoretical calculations have demonstrated that transition metal nitrides, including CrN, ZrN, and NbN, are potential candidates for NH₃ electrosynthesis under ambient conditions.^{24,25} Meanwhile, a nanoarray as the active component grown on a conductive matrix is favorable to enhance catalytic activity owing to the more exposed active sites and facilitated diffusion of the electrolyte and gas evolved.^{26–28} Therefore, it is highly attractive to develop the transition metal nitride nanoarray for the NRR, which, however, has not been reported.

In this communication, we demonstrate the development of a VN nanowire array grown on carbon cloth (VN/CC) as a highperformance catalyst for the NRR. Such an electrocatalyst achieves high ammonia yield ($2.48 \times 10^{-10} \text{ mol}^{-1} \text{ s}^{-1} \text{ cm}^{-2}$) and faradaic efficiency (3.58%) at -0.3 V versus RHE in 0.1 M HCl, outperforming most reported results for N₂ fixation under ambient conditions, and even comparing favourably to the yield and faradaic efficiency obtained under high temperatures and/or pressures.

The VN/CC nanowire array was synthesized *via* nitridation of a V_2O_5 nanowire array precursor. The scanning electron microscopy (SEM) images of V_2O_5 /CC with different magnifications show the well-coated nanowire array on CC (Fig. 1a). SEM images (Fig. 1b) suggest that the CC is completely covered with the VN nanowire array. The energy-dispersive X-ray (EDX) spectrum (Fig. S1, ESI[†]) for VN/CC further confirms the existence of V and N



College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, China. E-mail: fengliquhn@hotmail.com

[†] Electronic supplementary information (ESI) available: Experimental section and supplementary figures. See DOI: 10.1039/c8cc00459e



Fig. 1 SEM images for (a) V_2O_5/CC and (b) VN/CC. (c) TEM and HRTEM images for VN. (d) SEM and EDX elemental mapping images of V and N for VN/CC.

elements in the product. As shown in Fig. 1c, the transmission electron microscopy (TEM) image demonstrates that VN has a typical nanowire structure, and the high-resolution TEM (HRTEM) image taken from VN reveals well-resolved lattice fringes with an interplanar spacing of 0.207 nm, which corresponds to the (200) plane of VN. The SEM and corresponding energy-dispersive X-ray (EDX) elemental mapping images (Fig. 1d) suggest the uniform distribution of V and N elements.

Fig. 2a shows the X-ray diffraction (XRD) pattern for VN/CC. As observed, the peaks of VN/CC at 37.6° , 43.7° , 63.5° , and 76.2° are indexed to the (111), (200), (220), and (311) planes of VN (JCPDS No. 35-0768), respectively. Other peaks are typical diffraction peaks of CC. Fig. 2b shows the X-ray photoelectron spectroscopy (XPS) spectrum of VN, indicating the presence of

the elements V and N. In the V 2p region (Fig. 2c), the binding energies (BEs) at 513.5 and 521.2 eV are assigned to V 2p_{3/2} and V 2p_{1/2}²⁹ respectively. Meanwhile, the BEs at 515.5 and 528.3 eV are shakeup satellites.³⁰ In Fig. 2d, the N 1s spectrum shows a peak at 397.1 eV, corresponding to the BE of N in metal nitride.^{31,32} In the electrocatalytic process, N₂ gas is continually supplied in a feed stream to the VN/CC (loading: 1.59 mg cm^{-2}) cathode, where protons (H⁺ ions) transported through the electrolyte in 0.1 M HCl reacted with N2 to produce NH3. A schematic diagram of the reaction cell in this work is shown in Fig. 3a. The catalyst of VN/CC can provide suitable potentials to form ammonia via the Mars-van Krevelen mechanism, in which a nitrogen atom on the surface of VN was reduced to ammonia and the catalyst later regenerated with N2. Fig. 3b presents the UV-vis absorption spectra of the electrolyte stained with an indophenol indicator after electrolysis at different potentials for 3 h. This suggests that the highest absorbance intensity was measured at -0.3 V versus RHE. In this study, only NH₃ is detected without the by-product of N₂H₄. The concentration of the produced NH₃ is spectrophotometrically determined via the indophenol blue method,³³ while the produced N₂H₄ is estimated using the method of Watt and Chrisp.^{34,35} The calibration curves of detection are shown in Fig. S2 and S3 (see the ESI⁺), suggesting that VN/CC shows excellent selectivity for N2 reduction without N_2H_4 production (Fig. S4 and S5, ESI⁺). In Fig. S6 (ESI⁺), the UV-vis absorption spectra of VN/CC further confirm that the catalyst has excellent selectivity.

Fig. 3c shows the NH₃ yield and faradaic efficiency with the negative potential increasing until -0.3 V *versus* RHE, where the NH₃ yield and faradaic efficiency can reach the best values of 2.48×10^{-10} mol s⁻¹ cm⁻² and 3.58%, respectively. Beyond this negative potential, the NH₃ yield rate and faradaic efficiency decreased significantly, which was attributed to the competitive adsorption of N₂ and hydrogen species on the electrode



Fig. 2 (a) XRD pattern for VN/CC. (b) XPS survey spectrum for VN and XPS spectra in (c) V 2p and (d) N 1s.



Fig. 3 (a) Schematic reaction cell for the NRR. (b) UV-vis absorption spectra of the electrolytes stained with an indophenol indicator after VN/CC electrolysis at different potentials for 3 h. The potential started at -0.1 V and finished at -0.8 V. (c) Average NH₃ yields and faradaic efficiencies of VN/CC at different potentials. (d) Recycling test of VN/CC at the potential of -0.3 V *versus* RHE.



Fig. 4 (a) Time-dependent current density curves of VN/CC for the NRR at different potentials in 0.1 M HCl. (b) The SEM images for VN/CC after the stability test.

surface. As the catalytic potential was below -0.3 V versus RHE, the hydrogen evolution reaction becomes the primary process in this catalytic system. The NH₃ yield and faradaic efficiency of VN/CC are higher than those reported in previous literature, including Fe₂O₃/CNT (3.6 \times 10⁻¹² mol s⁻¹ cm⁻², 2.2% at -2.0 V),³⁶ Ru/C (3.43 \times 10⁻¹² mol s⁻¹ cm⁻², 0.28% at -1.1 V),³⁷ PEBCD/C (2.58 \times 10⁻¹¹ mol s⁻¹ cm⁻², 2.85% at –0.5 V), 38 and Mo nanofilms (3.09 \times 10^{-11} mol s $^{-1}$ cm $^{-2}$ at -0.49 V, 0.72% at -0.29 V).³⁹ Fig. 3d shows that the NH₃ yield and faradaic efficiency have no obvious variation during the recycling tests for 10 times, indicating that VN/CC has excellent repeatability for the NRR. Considering the stability is another significant parameter to evaluate the practicability of electrocatalysts, Fig. 4a shows the time-dependent current density curves at different potentials, which suggest that VN/CC can maintain its catalytic activity for at least 3 h. As shown in Fig. 4b, the SEM images of VN/CC after the stability test suggest that such a catalyst still preserves the original morphology. The XRD pattern is shown in Fig. S7 (ESI⁺), which shows that the diffraction peaks after the test are consistent with those of VN/CC before the test. And the XPS spectra indicated that the VN has no obvious change after the test (Fig. S8, ESI⁺).

In summary, a VN nanowire array has been successfully grown on CC (VN/CC), which is obtained from a V₂O₅ precursor *via* nitridation. As a high-efficient NRR catalyst in acidic media, it can obtain the NH₃ yield and faradaic efficiency of 2.48×10^{-10} mol s⁻¹ cm⁻² and 3.58%, respectively, as well as the excellent selectivity (no formation of N₂H₄) and durability in 0.1 M HCl. This work not only provides us an attractive catalyst material for the NRR in acidic media, but would also open up an exciting new avenue to the rational design and fabrication of transition metal nitrides for the NRR.

This work was supported by the National Natural Science Foundation of China (No. 21775089) and the Natural Science Foundation Projects of Shandong Province (No. ZR2017JL010 and ZR2017QB008).

Conflicts of interest

There are no conflicts of interest to declare.

References

- 1 K. A. Brown, D. F. Harris, M. B. Wilker, A. Rasmussen, N. Khadka, H. Hamby, S. Keable, G. Dukovic, J. W. Peters, L. C. Seefeldt and P. W. King, *Science*, 2016, 352, 448–450.
- 2 R. F. Service, Science, 2014, 345, 610.
- 3 M. A. H. J. van Kessel, D. R. Speth, M. Albertsen, P. H. Nielsen, H. J. M. Op den Camp, B. Kartal, M. S. M. Jetten and S. Lucker, *Nature*, 2015, **528**, 555–559.
- 4 G. Ertl, Angew. Chem., Int. Ed., 2008, 47, 3524-3535.
- 5 K. Honkala, A. Hellman, I. N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C. H. Christensen and J. K. Norskov, *Science*, 2005, 307, 555–558.
- 6 V. Rosca, M. Duca, M. T. de Groot and M. T. M. Koper, Chem. Rev., 2009, 109, 2209-2244.
- 7 S. Licht, B. Cui, B. Wang, F.-F. Li, J. Lau and S. Liu, Science, 2014, 345, 637–640.
- 8 C. J. M. van der Ham, M. T. M. Koper and D. G. H. Hetterscheid, *Chem. Soc. Rev.*, 2014, **43**, 5183–5191.
- 9 R. Michalsky, A. M. Avram, B. A. Peterson, P. H. Pfromm and A. A. Peterson, *Chem. Sci.*, 2015, **6**, 3965–3974.
- 10 R. Michalsky, A. M. Avram, B. A. Peterson, P. H. Pfromm and A. A. Peterson, *Chem. Sci.*, 2015, **6**, 3965–3974.
- 11 I. Rafiqul, C. Weber, B. Lehmann and A. Voss, *Energy*, 2005, 30, 2487–2504.
- 12 M. Jewess and R. H. Crabtree, ACS Sustainable Chem. Eng., 2016, 4, 5855–5858.
- 13 K. C. Macleod and P. L. Holland, Nat. Chem., 2013, 5, 559-565.
- 14 J. Kim and D. C. Rees, Nature, 1992, 360, 553-560.
- 15 T. Murakami, T. Nishikiori, T. Nohira and Y. Ito, J. Am. Chem. Soc., 2003, **125**, 334–335.
- 16 R. Schlögl, Angew. Chem., Int. Ed., 2003, 42, 2004-2008.
- 17 H. Broda and F. Tuczek, Angew. Chem., Int. Ed., 2014, 53, 632-634.
- 18 N. Cherkasov, A. O. Ibhadon and P. Fitzpatrick, *Chem. Eng. Process.*, 2015, **90**, 24–33.
- 19 V. Kyriakou, I. Garagounis, E. Vasileiou, A. Vourros and M. Stoukides, *Catal. Today*, 2016, 286, 2–13.
- 20 G. Marnellos and M. Stoukides, Science, 1998, 282, 98-100.
- 21 W. Wang, X. Cao, W. Gao, F. Zhang, H. Wang and G. Ma, *J. Membr. Sci.*, 2010, **360**, 397–403.
- 22 S.-J. Li, D. Bao, M.-M. Shi, B.-R. Wulan, J.-M. Yan and Q. Jiang, Adv. Mater., 2017, 29, 1700001.
- 23 K. Kugler, M. Luhn, J. A. Schramm, K. Rahimi and M. Wessling, *Phys. Chem. Chem. Phys.*, 2015, **17**, 3768–3782.
- 24 Y. Abghoui, A. L. Garden, J. G. Howalt, T. Vegge and E. Skulason, ACS Catal., 2016, 6, 635–646.
- 25 Y. Abghoui and E. Skúlasson, Procedia Comput. Sci., 2015, 51, 1897-1906.
- 26 X. Zhang, C. Si, X. Guo, R. Kong and F. Qu, J. Mater. Chem. A, 2017, 5, 17211–17215.
- 27 H. Du, X. Zhang, Q. Tan, R. Kong and F. Qu, *Chem. Commun.*, 2017, 53, 12012–12015.
- 28 X. Guo, R.-M. Kong, X. Zhang, H. Du and F. Qu, ACS Catal., 2018, 8, 651–655.
- 29 D. Zhao, Z. Cui, S. Wang, J. Qin and M. Cao, J. Mater. Chem. A, 2016, 4, 7914–7923.
- 30 C. Ji, J. Bi, S. Wang, X. Zhang and S. Yang, J. Mater. Chem. A, 2016, 4, 2158–2168.
- 31 N. Fechler, T.-P. Fellinger and M. Antonietti, *Chem. Mater.*, 2012, 24, 713–719.
- 32 B. Koscielska, A. Winiarski and W. Jurga, *J. Non-Cryst. Solids*, 2010, **356**, 1998–2000.
- 33 D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nat. Mater.*, 2013, 12, 836–841.
- 34 M.-M. Shi, D. Bao, B.-R. Wulan, Y.-H. Li, Y.-F. Zhang, J.-M. Yan and Q. Jiang, Adv. Mater., 2017, 29, 1606550.
- 35 D. Bao, Q. Zhang, F.-L. Meng, H.-X. Zhong, M.-M. Shi, Y. Zhang, J.-M. Yan, Q. Jiang and X.-B. Zhang, *Adv. Mater.*, 2017, 29, 1604799.
- 36 S. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. Su and G. Centi, Angew. Chem., Int. Ed., 2017, 56, 2699–2703.
- 37 V. Kordali, G. Kyriacou and Ch. Lambrou, *Chem. Commun.*, 2000, 1673–1674.
- 38 G.-F. Chen, X. Cao, S. Wu, X. Zeng, L.-X. Ding, M. Zhu and H. Wang, J. Am. Chem. Soc., 2017, 139, 9771–9774.
- 39 D. Yang, T. Chen and Z. Wang, J. Mater. Chem. A, 2017, 5, 18967-18971.